PB-230 275

METHOD RESEARCH STUDY 3, DEMAND ANALYSES. AN EVALUATION OF ANALYTICAL METHODS FOR WATER AND WASTEWATER

J. A. Winter

National Environmental Research Center
Cincinnati, Ohio

1971

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PB 230 275

METHOD RESEARCH STUDY 3, DEMAND ANALYSES

An Evaluation of Analytical Methods for Water and Wastewater

1971

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Analytical Quality Control Laboratory
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ACKNOWLEDGEMENTS

The author acknowledges the technical assistance and guidance of Mr. Elmo C. Julian, Analytical Quality Control Laboratory, National Environmental Research Center, Cincinnati, in the design, development and operation of the statistical computer programs used in this study.

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PARTICIPATING LABORATORIES

Eighty-six analysts in 58 laboratories took part in *Method Research Study 3, Demand Analyses*. Of the 58 laboratories, 40 were non-EPA. The participating laboratories were:

EPA Laboratories

Advanced Waste Treatment Plant
D. C. Pollution Control Plant
Washington, D. C.

Advanced Waste Treatment
Research Laboratory
Cincinnati, Ohio

Alaska Water Laboratory
College, Alaska

Baton Rouge Field Facility
Baton Rouge, Louisiana

California-Nevada Basins Sub-Region
Alameda, California

Cincinnati Field Investigations Center
Cincinnati, Ohio

Edison Water Quality Laboratory
Edison, New Jersey

Illinois District Office
Chicago, Illinois

Indiana District Office
Evansville, Indiana

Missouri Basin Laboratory
Kansas City, Missouri

National Environmental Research Center
Corvallis, Oregon

New England Basin Office
Needham Heights, Massachusetts

Pomona Pilot Plant
Pomona Water Reclamation Plant
Pomona, California

Solid Waste Research Division
Cincinnati, Ohio

R. S. Kerr Water Research Center
Research
Ada, Oklahoma

R. S. Kerr Water Research Center
Technical Programs
Ada, Oklahoma

Southeast Water Laboratory
Athens, Georgia

Wheeling Field Station
Wheeling, West Virginia

Non-EPA Laboratories

California State Dept. of Public Health
Sanitation and Radiation Laboratory
Berkeley, California

California State Dept. of Public Health
Southern California Laboratory
Los Angeles, California

California Dept. of Water Resources
Sacramento, California

City of Chicago Dept. of Water & Sewers
Water Purification Laboratory
Chicago, Illinois

Clark County Sanitation Districts
Las Vegas, Nevada

Colorado Springs Waste Water Treatment
Colorado Springs, Colorado

Commonwealth of Massachusetts
Lawrence Experimental Station
Lawrence, Massachusetts

E. I. du Pont de Nemours & Co., Inc.
Belle, West Virginia

Environmental Quality Control Commission
Portland, Oregon

FMC Corporation
Inorganics Division
South Charleston, West Virginia

FMC Corporation
Organic Chemicals Division
Nitro, West Virginia

FMC Corporation
Viscose Division
Nitro, West Virginia

Houston City Health Department
Houston, Texas

Hyperion Treatment Plant
Playa del Rey, California

Idaho State Health Department
Boise, Idaho

Indiana State Board of Health
Indianapolis, Indiana

International Paper Company
Springhill, Louisiana

Interstate Sanitation Commission
New York, N. Y.

Kansas City Water Department
Kansas City, Missouri

Los Angeles Dept. of Water
and Power
Los Angeles, California

Metropolitan Denver Sewage Disposal
Commerce City, Colorado

Maryland State Dept. of
Water Resources
Annapolis, Maryland

Metropolitan Sanitary District
of Greater Chicago
Cicero, Illinois

Miami Conservancy District
Dayton, Ohio

Middlesex County Sewerage Authority
Sayreville, New Jersey

Monsanto Chemical Company
Organic Chemicals Division
Nitro, West Virginia

North Carolina Dept. of Water
and Air Resources
Raleigh, North Carolina

Ohio Dept. of Health
Columbus, Ohio

Pennsylvania Dept. of Health
and Welfare
Harrisburg, Pennsylvania

Santee County Water District
Santee, California

Sewerage and Water Board
New Orleans, Louisiana

South Carolina Pollution Control
Authority
Columbia, South Carolina

South Tahoe Public Utilities District
South Lake Tahoe, California

Texas A & M University
Environmental Engineering Division
College Station, Texas

Union Carbide Corporation
Olefins Division
South Charleston, West Virginia

Union Carbide Corporation
Organics Division
Charleston, West Virginia

Water & Air Resources Commission
Dover, Delaware

Water Pollution Control Commission
Olympia, Washington

West Virginia Dept. of Natural
Resources
Charleston, West Virginia

Virginia State Water Control
Board
Richmond, Virginia

METHOD RESEARCH STUDY 3, DEMAND ANALYSES

An Evaluation of Analytical Methods for Water and Wastewater

SUMMARY

The Analytical Quality Control Laboratory of National Environmental Research Center, Environmental Protection Agency, conducted interlaboratory research studies on selected chemical methods of analysis for chemical oxygen demand(COD), total organic carbon (TOC) and for biochemical oxygen demand (BOD). Sample concentrates were prepared at low (natural water) levels and at higher (municipal waste) levels for each constituent. Analysts added an aliquot of each concentrate to distilled water for COD and TOC analyses and to a natural water of their choice for BOD analyses. Single analyses were made on the distilled and natural water samples with and without added increments. Recoveries were compared. The bias of the method and, where possible, the interference of natural water samples and the relative precision of each analyst and laboratory were determined. A statistical summary of this data on page *viii* shows the precision and accuracy values which may be expected in routine work.

A Statistical Summary of Method Research Study 3, Demand Analyses

Chemical Oxygen Demand Analyses of Distilled Water Samples		
True Value, mg COD/liter	12.3	270
Mean of Recoveries by Difference, mg COD/liter	12.34	257.4
Accuracy as % Relative Error (Bias)	0.3	-4.7
Standard Deviation, mg COD/liter	4.15	17.76
Relative Deviation, %	33.6	6.9
Range, mg COD/liter	25.3	104

Biochemical Oxygen Demand Analyses of Distilled/Seeded and Natural Water Samples		
True Value, mg BOD/liter	2.2	194
Mean of Recoveries by Difference, mg BOD/liter	2.12	175
Accuracy as % Relative Error (Bias)	-3.7	-9.8
Standard Deviation mg BOD/liter	0.7	26.
Relative Deviation, %	33.2	15.0
Range, mg BOD/liter	5.5	118

Total Organic Carbon Analyses of Distilled Water Samples		
True Value, mg TOC/liter	4.9	107
Mean of Recoveries by Difference, mg TOC/liter	5.65	108.1
Accuracy as % Relative Error (Bias)	15.3	1.0
Standard Deviation, mg TOC/liter	1.89	6.
Relative Deviation, %	33.5	5.6
Range, mg TOC/liter	10.2	33

METHOD RESEARCH STUDY 3, DEMAND ANALYSES
An Evaluation of Analytical Methods for Water and Wastewater

INTRODUCTION

The Office of Research and Monitoring, EPA, gathers water and air quality data, and makes noise and solid wastes measurements, to determine compliance with established environmental standards, to provide information for planning natural resources development, to determine the effectiveness of pollution abatement procedures and to assist in research activities. As a help in achieving these goals, EPA Administrator, William D. Ruckelshaus, recently established National Environmental Research Centers (NERC) at Cincinnati, Ohio, Corvallis, Oregon, and Research Triangle Park, North Carolina.

In a large measure the success of these environmental protection efforts rests upon the reliability of the information provided by the data collection activities. Therefore, the Analytical Quality Control Laboratory (AQCL) was established as part of the National Environmental Research Center, Cincinnati, to insure the reliability of physical, chemical, biological and microbiological water quality data generated and, when necessary, to insure the legal defensibility of all such environmental quality information collected by the Agency.

The Method and Performance Evaluation Activity of AQCL conducts evaluative interlaboratory research studies of analytical procedures used in the Research and Monitoring Office, EPA. In this study the demand parameters, chemical oxygen demand (COD), total organic carbon (TOC), and biochemical oxygen demand (BOD), were tested to measure the accuracy and precision of the selected methods used in participating laboratories. The evaluation of results also permits a judgment of the relative capabilities of these laboratories performing these analyses.

DESCRIPTION OF STUDY

Test Design

A simple test design was used in this study of demand parameters. Each sample was prepared as a stable concentration in a sealed glass ampul. When an aliquot of the concentrate was diluted to volume, constituents were present at levels found in natural waters or sewage.

An aliquot from each ampul was diluted to volume with distilled water for COD and TOC analysis and with distilled/seeded or natural water for BOD analysis.

Preparation of Samples and Reporting of Results

Two water sample concentrates were prepared for Method Study 3 by dissolving weighed amounts of reagent-grade chemicals in ASTM reagent-grade distilled water to produce accurately-known concentrations of COD, BOD and TOC.

The concentrates were preserved by steam sterilization and were checked for stability by repeated analyses over a period of three months. These analyses established that the solutions were stable and verified the concentration of each constituent. Further confirmation of the *true values* was obtained from determinations by an independent referee laboratory. These calculated *true values* verified by analyses are shown in Table 1.

Table 1. True Values for Demand Parameters

When diluted in distilled water according to instructions, the water samples contained the following concentrations of constituents, mg/liter:

Parameter	Sample 1	Sample 2
Organic Carbon[1)]	4.85	107
Chemical Oxygen Demand[2)]	12.3	270
Biochemical Oxygen Demand[3)]	2.2	194

[1)] The calculated theoretical levels of organic carbon produced in these samples by dissolving the weighed amounts of high purity reagents in distilled water.

[2)] The calculated theoretical COD values obtained by complete oxidation of the samples to carbon dioxide, water, and ammonia. In actual practice, the theoretical values are very difficult to attain.

[3)] The concentrations given for BOD are theoretical demands based on reported values in *Standard Methods* using river water as seed (1). These values may or may not be reproducible in a specific laboratory because of natural variability of the seed organisms from sample to sample.

Each analyst was instructed to dilute a separate 5.0 ml aliquot of each concentrate to one liter with ammonia-free water or with river, lake or estuarine water. Distilled water was used as the diluent for the COD and TOC tests to avoid the extreme variability in data which might arise from the inhibitive or exhibitive effects of the organic waste content of individual waters. For COD and TOC tests, a result was obtained for distilled water plus the increment. Natural water was used as the seed source and/or diluent for the BOD test. Recovery of the BOD increment in natural water was determined by difference from the natural water BOD. The sample concentrates were shipped to participating laboratories in November, 1969 with detailed instructions for analysis and the reporting of results within thirty days.

Analytical Methods

The analyses were performed according to the *FWPCA Methods for Chemical Analysis of Water and Wastes*, November, 1969. The methods used for these analyses were referenced as follows:

Parameter	Basic Reference
Chemical Oxygen Demand	*Standard Methods for the Examination of Water and Wastewater*, 12th ed., APHA, Inc., N. Y., 1965, 510-514. *Book of ASTM Standards*, Part 23, 1969 Water; Atmospheric Analysis, pp. 243-246.
Biochemical Oxygen Demand	*Standard Methods for the Examination of Water and Wastewater*, 12th ed., APHA, Inc., N. Y., 1965, 415-421. *Book of ASTM Standards*, Part 23 1969, Water; Atmospheric Analysis, pp. 715-723.
Total Organic Carbon	*Book of ASTM Standards*, Part 23, 1969 Water; Atmospheric Analysis, pp. 826-830.

Glossary of Terms

The statistical measurements used in this report are defined as follows:

Accuracy as % Relative Error (Bias). The signed difference between mean value and the true value, expressed as a percent of the true value.

$$R.\ E. = \frac{X_{true} - \overline{X}}{X_{true}} \times 100$$

Confidence Limit (95%). The range of values within which a single analysis will be included, 95% of the time.

$$C.\ L. = \overline{X} \pm t\ \frac{\sigma}{n}$$

where t = value from t table, σ = standard deviation and n = number of samples.

Mean ($\overline{X}$). The arithmetic mean of reported values, the average.

Median. Middle value of all data ranked in ascending order. If there are two middle values, the mean of these values.

n. The number of sets of values or analysts reported in a study.

Range. The difference in mg/liter between lowest and highest reported values.

Relative Deviation (Coefficient of Variation). The ratio of the standard deviation, σ, of a set of numbers to their mean, $\overline{X}$, expressed as percent. It is an attempt to relate the deviation (precision) of a set of data to the size of n so that the deviations for differing levels of a parameter can be compared fairly.

$$R.\ D. = 100\ \frac{\sigma}{\overline{X}}$$

Skewness (k). A pure number, positive or negative, which indicates the lack of symmetry in a distribution, For example, k is positive if the distribution tails to the right and negative if the distribution tails to the left.

$$\underline{k} = \frac{\Sigma\ (X_i - \overline{X})^3}{n\sigma^3}$$

Standard Deviation (σ). The most widely used measure of dispersion of a set of data. σ is equal to the square root of the variance and with normal distribution indicates the deviation of 68% of the values around the mean, while 1.96σ indicates the deviation of 95% of the values around the mean. The *standard deviation*, σ, is the measure of the deviation of the universe. However, in most experimental work with limited sampling and in this study only an *estimated standard deviation*, s is measurable. The calculation differs in that n-1 rather than n is used as the denominator. In this study and in further studies, s and s^2 not σ and σ^2 will be used to estimate the deviation of the data. They will be referred to as the *standard deviation* and *variance* respectively.

$$\sigma = \sqrt{\frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n}}$$

t-test. The difference in analyzed and true value expressed as ratio over the *standard deviation*. The value obtained is compared with critical values in a table. If the calculated t-value exceeds the theoretical t-value, the analyzed value is probably not from the same population as the rest of the data and can be rejected.

$$\text{t-value} = \frac{X_n - \text{true value}}{\textit{Standard Deviation } (s)}$$

True Value. Those amounts actually added in sample preparation. These are not based on analyses, the latter being used only for verification.

Variance (σ^2), (s^2). The average of the squares of the deviations of a group of numbers from their average, $\bar{X}$.

$$\sigma^2 = \frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n} \qquad s2 = \frac{\Sigma X_i^2 - \frac{(\Sigma X_i)^2}{n}}{n-1}$$

RESULTS

Raw Data

Direct copies of the computer printout showing all test results reported by participating laboratories are given by parameter in the APPENDIX.

TREATMENT OF DATA

Statistical Summary

Complete statistical summaries are given in pages 10 thru 19. Each parameter is discussed in turn with data displayed and statistically evaluated for each concentration. For ease in presentation and to prevent round-off errors, five decimal places were carried in all measurements, however, the number of significant figures is only equal to the number reported for the increment.

A program described by Larsen (3) was modified for an IBM 1130 computer and measurement of accuracy and presentation of ranked data were added. This summary display named COLST provides all of the statistical measurements necessary for evaluation of the data as a direct copy of the computer printout. With the exception of accuracy, all measurements (*number of values, true value, mean, median, accuracy, range, variance, standard deviation, 95% confidence limit, relative deviation* (coefficient of variation) and *skewness*) are based on all data received, without rejection. Because the inclusion of questionable extreme values will result in unreasonable values for accuracy, the *accuracy* values for COD, BOD and TOC are based on retained data, that is, the data remaining after rejection of outliers using the *t-test* at the 99% level. In addition to the statistical measurements, all data are ranked in ascending order and presented in a histogram, using $n = \sqrt{s.d.}$ cell divisions. Each X in the histogram represents one analytical

result for up to 15 values/cell. When more than 15 values occur per cell only 15 X's are printed and the number of values actually included is indicated by the number at the base of each cell. The distribution of X values characterizes the method as used on these natural water samples.

Although it is not possible to calculate a BOD result independently of the seed material, it is necessary to use a *true value* to obtain some measure of accuracy. In this study BOD values were calculated from a table of these values for river water given in *Standard Methods* (1).

Rejection of Outliers

To determine the accuracy of each method, it was necessary to remove those extreme values which had only a small chance of validity and which would make a significant change in the accuracy measure. These values were probably caused by gross instrumental, chemical or human error. The extreme values were rejected by applying the two-tail *t-test* to all values at a 99% probability level, that is, with a 99 to 1 assurance that the data rejected were invalid and should be rejected. The data points rejected are indicated with a capital letter, "R", after the values in the Figures and in the data tabulations in the Appendix. A greater spread of data around the true value causes rejection of fewer outliers. As the standard deviation of the method increases in the denominator of the *t-test*, the calculated *t* value grows smaller and there are fewer extreme values rejected as outliers.

DISCUSSION

Chemical Oxygen Demand (Dichromate Oxygen Demand)

COD Level, 12.3 mg/liter

The evaluation of the COD test at low level of organic demand is shown on page 10. The COD method had only .3% bias. The data distribution was normal but a number of laboratories had some difficulty as indicated by a standard deviation of 4.15 mg/liter at this low level. There is a 95% probability that analysis of a COD sample containing 12 mg/liter will vary 8.13 mg/liter or 66% about the mean.

COD Level, 270 mg/liter

The statistical summary on page 11 shows COD test results at the 200-300 mg/liter level expected in municipal sewage. The accuracy is expressed as a negative bias of 4.7%, equivalent to 13 mg/liter at the 270 mg/liter level. The precision of the COD method was improved at this 270 mg/liter level to a standard deviation of 17.8 mg/liter. This is equivalent to a 35 mg/liter variation about the mean at the 95% confidence interval.

Summary of COD Analyses

The COD test showed a relatively low bias of 0.3% and 4.7% at levels of 12 and 270 mgCOD/liter levels respectively. However, the COD test was less precise at a low demand level, showing a 33% relative deviation in analysis of 12 mg/liter level as compared with a 7% deviation about the mean in analysis of the 270 mg/liter level.

METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

COD, SAMPLE 1

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 12.3

N	86	RANGE	25.30000	COEF. VAR.	0.33631
TRUE VAL.	12.3	VARIANCE	17.22591	SKEWNESS	0.85772
MEAN	12.34066	STD. DEV.	4.15041	NO. OF CELLS	9
MEDIAN	12.00000	CONF. LIM.	8.13480 (95 PCT)		
ACCURACY	0.33062	PCT RELATIVE ERROR, RETAINED DATA			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ	HISTOGRAM
1.2R	11.4	14.8	1.2000	1	X
4.0	11.5	14.8	4.3625	2	XX
5.8	11.6	15.2	7.5249	9	XXXXXXXXX
6.2	11.6	15.4	10.6875	37	XXXXXXXXXXXXXXX
6.3	11.7	16.6	13.8499	25	XXXXXXXXXXXXXX
6.7	11.7	16.9	17.0124	5	XXXXX
6.8	12.0	17.2	20.1749	3	XXX
7.3	12.0	17.4	23.3374	3	XXX
7.4	12.0	17.8	26.4999	1	X
7.8	12.0	18.9			
8.0	12.2	19.4			
8.1	12.2	21.7			
9.4	12.2	22.8			
9.6	12.2	22.9			
9.8	12.3	24.0R			
9.9	12.3	26.5R			
10.0	12.4				
10.1	12.5				
10.2	12.5				
10.2	12.5				
10.4	12.5				
10.7	12.5				
10.7	12.6				
10.7	12.6				
10.8	12.7				
10.8	12.8				
10.9	12.9				
11.0	13.0				
11.2	13.1				
11.3	13.2				
11.3	13.4				
11.3	13.9				
11.3	14.1				
11.4	14.3				
11.4	14.6				

R = REJECTED DATA.

METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

COD, SAMPLE 2

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 270.

N	82	RANGE	104.00001	COEF. VAR.	0.06900
TRUE VAL.	270.	VARIANCE	315.39721	SKEWNESS	-1.14857
MEAN	257.37805	STD. DEV.	17.75942	NO. OF CELLS	9
MEDIAN	261.00006	CONF. LIM.	34.80847 (95 PCT)		
ACCURACY	-4.67481	PCT RELATIVE ERROR, RETAINED DATA			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ	HISTOGRAM
198.R	259.	270.	198.0000	1	X
205.R	260.	272.	211.0000	3	XXX
208.R	260.	274.	224.0000	3	XXX
215.R	260.	274.	237.0000	5	XXXXX
220.R	260.	275.	250.0000	16	XXXXXXXXXXXXXXX
221.R	261.	276.	263.0000	42	XXXXXXXXXXXXXXX
222.R	261.	277.	276.0000	9	XXXXXXXXX
237.	261.	279.	289.0000	2	XX
238.	262.	279.	302.0000	1	X
239.	262.	286.			
240.	263.	289.			
243.	263.	302.			
244.	263.				
245.	263.				
246.	264.				
248.	264.				
250.	264.				
250.	264.				
251.	264.				
252.	264.				
253.	264.				
253.	265.				
253.	265.				
253.	265.				
254.	266.				
255.	267.				
255.	267.				
256.	267.				
257.	267.				
257.	267.				
257.	268.				
257.	268.				
258.	269.				
258.	269.				
259.	269.				

R = REJECTED DATA.

Biochemical Oxygen Demand (BOD)

BOD Level, 2.2 mg/liter

The BOD test had negligible bias at this low level common to many natural waters. In this study, analysts were instructed to bring the aliquot up to volume with distilled water and/or a natural water or domestic sewage in sufficient amounts to provide ample seed. Although the seventy-three analysts used as many different sources of natural water and/or sewage as seed, the data on page 13 showed a negative bias of only 3.75%. The standard deviation of 0.7 mg/liter was 33% of the level tested. This is the same relative deviation as was obtained with the TOC test on the same sample. At this low 2 mg/liter level, BOD data will deviate 1.4 mg/liter about the mean at 95% confidence interval.

BOD Level, 194 mg/liter

At this higher level of organic loading which is similar to a municipal sewage, the BOD test results on page 14 show a negative bias of 9.8%. The standard deviation of 26 mg/liter for BOD is more than that of the COD or TOC tests at this level. The BOD results can be expected to deviate 52 mg/liter about the mean, with a 95% confidence.

Summary of BOD Analyses

Although the BOD test is non-standard because of the inability to control the most important "reagent" in the test, the microorganisms used as seed material, the results of this study indicate that the test is capable of reasonable accuracy and precision when a replicate synthetic non-toxic sample is the substrate. However, in routine analyses of environmental samples, one always needs to verify the accuracy of the BOD result because of the varying ability of different seeds to fully oxidize the sample and the possible toxic effect of the substrate tested.

METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

BOD, SAMPLE 1

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM SEEDED WATER

INCREMENT = 2.2

N	74	RANGE	5.50000	COEF. VAR.	0.33193
TRUE VAL.	2.2	VARIANCE	0.49406	SKEWNESS	1.80488
MEAN	2.11756	STD. DEV.	0.70290	NO. OF CELLS	8
MEDIAN	2.10000	CONF. LIM.	1.37768 (95 PCT)		
ACCURACY	-3.74713	PCT RELATIVE ERROR, RETAINED DATA			

DATA IN ASCENDING ORDER			MIDPOINT	FREQ	HISTOGRAM
0.3R	2.1	3.2	0.3000	1	X
1.0	2.1	3.5	1.0857	7	XXXXXXX
1.0	2.1	3.7	1.8714	39	XXXXXXXXXXXXXXX
1.0	2.1	5.8R	2.6571	23	XXXXXXXXXXXXXXX
1.1	2.1		3.4428	3	XXX
1.2	2.2		4.2285	0	
1.3	2.2		5.0142	0	
1.4	2.2		5.7999	1	X
1.5	2.2				
1.5	2.2				
1.6	2.2				
1.6	2.2				
1.6	2.3				
1.6	2.3				
1.6	2.3				
1.7	2.3				
1.8	2.3				
1.8	2.3				
1.8	2.3				
1.8	2.3				
1.8	2.4				
1.9	2.4				
1.9	2.4				
1.9	2.4				
2.0	2.5				
2.0	2.5				
2.0	2.5				
2.0	2.5				
2.0	2.6				
2.0	2.6				
2.0	2.6				
2.0	2.6				
2.0	2.7				
2.0	2.8				
2.0	3.0				

R = REJECTED DATA.

METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

BOD, SAMPLE 2

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM SEEDED WATER

INCREMENT = 194.

N	73	RANGE	118.00001	COEF. VAR.	0.14975
TRUE VAL.	194.	VARIANCE	686.80566	SKEWNESS	-0.49208
MEAN	175.00003	STD. DEV.	26.20697	NO. OF CELLS	8
MEDIAN	179.00003	CONF. LIM.	51.36566 (95 PCT)		
ACCURACY	-9.79381	PCT RELATIVE ERROR, RETAINED DATA			

DATA IN ASCENDING ORDER

107.R	175.	223.
118.R	179.	224.
120.R	179.	225.
121.R	180.	
123.R	180.	
130.	181.	
132.	182.	
135.	183.	
142.	183.	
145.	183.	
146.	185.	
150.	185.	
152.	185.	
154.	188.	
155.	189.	
155.	190.	
159.	191.	
159.	191.	
160.	192.	
164.	192.	
165.	193.	
165.	194.	
167.	197.	
168.	197.	
169.	198.	
169.	200.	
170.	200.	
171.	201.	
171.	203.	
172.	205.	
172.	205.	
173.	205.	
174.	205.	
174.	207.	
175.	218.	

MIDPOINT	FREQ	HISTOGRAM
107.0000	1	X
123.8571	6	XXXXXX
140.7142	4	XXXX
157.5714	11	XXXXXXXXXXX
174.4285	20	XXXXXXXXXXXXXXX
191.2856	18	XXXXXXXXXXXXXXX
208.1427	9	XXXXXXXXX
224.9998	4	XXXX

R = REJECTED DATA.

Total Organic Carbon (TOC) by Combustion-Infrared Analysis

The instrument for these TOC analyses is a single or dual furnace with air pump, purification train, flow controls, non-dispersive type infrared stream analyzer sensitized specifically for carbon dioxide, and a recorder (4).

TOC Level, 5 mg/liter

At this low level of organic carbon, the TOC method results on page 18 show a significant 15% positive bias, that is, the average result was 15% higher than the true value. Furthermore, results at this level deviate 33% about the mean TOC result of 5.6 mg/liter. At the 95% confidence level, these low TOC values can be expected to deviate 3.7 mg/liter about the mean.

TOC Level, 100 mg/liter

At the higher municipal waste level of 100 mg TOC/liter, the TOC results on page 19 showed greatly improved accuracy, with the bias reduced to 1%. The standard deviation was reduced also to 6.0% of the level tested. At the 100 mg/liter level, TOC values can be expected to deviate 11-12 mg/liter about the mean values with a 95% probability.

Summary of TOC Analyses

The Total Organic Carbon test as performed on a Dow/Beckman Carbon Analyzer or similar instrument had limited precision and accuracy at the low (5 mg/liter) level. When samples contain organic carbon at levels equivalent to municipal wastes, accuracy was improved to a 1% positive bias and the relative standard deviation was reduced to 5-6% of the level tested.

Since the same technique and the same microsyringes are used to inject the samples with low and high levels of organic matter, the same systematic error should exist for both, with the exception that the sample containing the higher level of organic carbon should have the added variability of dilution. Although the specific cause of this imprecision at low levels cannot be isolated here, it is most probably one or more of the following factors:

1) Differences in the range settings used by the analysts for TOC analyses, e.g., 1-30 mg, 1-100 mg or 1-1000 mg/liter at full range.
2) Differences in the volume of sample injected, i.e., use of a 20 µl, 40 µl or 100 µl syringe.
3) Individual differences in injection techniques.
4) Variable use of dilution technique to reduce high level TOC sample before analysis.
5) Variable performance of needles, combustion systems and detectors in the carbon analyzer instruments.

Because the EPA method research studies are intended to evaluate analytical methods as they are used routinely in the field, little guidance was given on technique other than furnishing the written analytical method and informing the analyst of the range of the samples. Using basic instructions, the analyst did the measurement to the best of his ability.

There are chances for error in the TOC test which are unique among the three oxygen demand tests. For example, injection of 40 µl volume sample containing a 10 mg/liter level of TOC really involves a measurement on only 0.4 µg of carbon. A very slight contamination by dust, lint, cellulose, etc. is enough to add a relatively large positive error. Similarly, small inaccuracies in volumetric measurement could cause detectable error because the error would be magnified by the large factor necessary to convert a

µg/liter measurement to mg/liter in the final value.

We conclude that extreme care must be used operating the carbon analyzer (Dow-Beckman type). Despite the availability of instrumentation and a relatively good precision for the method reported in a single laboratory study, data from this group of laboratories shows a significant increase in variability. Apparently there is a lack of uniformity in the techniques used by these laboratories. Use of automatic injection devices or syringes should increase reproducibility.

METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

TOC, SAMPLE 1

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 4.9

N	27	RANGE	10.20000	COEF. VAR.	0.33522
TRUE VAL.	4.9	VARIANCE	3.58489	SKEWNESS	3.28807
MEAN	5.64814	STD. DEV.	1.89338	NO. OF CELLS	5
MEDIAN	5.00000	CONF. LIM.	3.71102 (95 PCT)		
ACCURACY	15.26828	PCT RELATIVE ERROR, RETAINED DATA			

DATA IN ASCENDING ORDER	MIDPOINT	FREQ	HISTOGRAM
3.8	3.8000	16	XXXXXXXXXXXXXXX
4.0	6.3500	10	XXXXXXXXXX
4.2	8.8999	0	
4.3	11.4499	0	
4.5	13.9999	1	X
4.7			
5.0			
5.0			
5.0			
5.0			
5.0			
5.0			
5.0			
5.0			
5.0			
5.0			
5.4			
5.7			
6.0			
6.0			
6.3			
6.4			
6.5			
6.5			
7.0			
7.2			
14.0R			

R = REJECTED DATA.

METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

TOC, SAMPLE 2

STATISTICS, ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 107.

N	26	RANGE	33.00000	COEF. VAR.	0.05551
TRUE VAL.	107.	VARIANCE	35.99380	SKEWNESS	0.74660
MEAN	108.07693	STD. DEV.	5.99948	NO. OF CELLS	5
MEDIAN	107.50001	CONF. LIM.	11.75898 (95 PCT)		
ACCURACY	1.00646	PCT RELATIVE ERROR, RETAINED DATA			

DATA IN ASCENDING ORDER	MIDPOINT	FREQ	HISTOGRAM
94.	94.0000	1	X
100.	102.2500	8	XXXXXXXX
102.	110.5000	15	XXXXXXXXXXXXXXX
103.	118.7500	1	X
104.	127.0000	1	X
104.			
105.			
106.			
106.			
107.			
107.			
107.			
107.			
108.			
110.			
110.			
110.			
110.			
110.			
110.			
110.			
110.			
112.			
114.			
117.			
127.R			

R = REJECTED DATA.

CONCLUSIONS

The Office of Research and Monitoring, EPA, gave careful consideration to the methods for measuring the oxygen demand of materials in waters, before selection of methods for the EPA manual, *Methods for Chemical Analysis of Water and Wastes*, 1971.

Three oxygen demand methods were selected for use in EPA: the Chemical Oxygen Demand (COD) Test, the Biochemical Oxygen Demand (BOD) Test, and the Total Organic Carbon (TOC) Test. BOD was included because of its historic use; however, the EPA manual points out that the extreme differences in the microorganisms used a seed and the variable biodegradability of chemical substances, makes the BOD a non-standard test (5). ASTM's Subcommittee D-19 has recommended withdrawal of the BOD test as a standard test because of these same difficulties in its use (6). However, these variables also make the BOD Test unique. It is the only test of the three that measures the amount of oxygen used by selected microorganisms in stabilizing the substances under test.

This study was designed to measure the effectiveness of the three oxygen demand methods in degrading a test substance. The oxidation used differed for each of the three methods. By using a test substrate which was completely degradable for all three methods, the study measured variability in the methods and analysts rather than variability in degradation of the sample.

In this study the three methods of measuring oxygen demand had similar accuracy and precision. The COD Test was most accurate at the low level with a 0.3% bias and the TOC Test was most accurate at the high level with a 1% bias.

Although true values for oxygen demand ranged from 2-12 mg/liter for COD, BOD and TOC analyses on the same low level sample, the relative deviation of the three tests was an identical 33%, indicating that these deviations were caused by imprecision in the methods not differences in the 2-12 mg/liter level of oxygen demand present. At the higher level of oxygen demand, the TOC and the COD tests were similar with 5.6% and 6.9% relative deviation, respectively.

The similar precision statements for COD, BOD and TOC at the low level (1-10 mg/liter) support the contention that a major factor in precision of demand analyses is the level tested. Regardless of the method, good precision is difficult to achieve. At the higher levels, all methods improved, with COD and TOC showing both increased precision and increased accuracy. This study has also shown that when controls are exerted over methodology and some uniformity is followed in the seed usage, the BOD results on a replicate biodegradable sample are reasonable.

However, the accurate and precise performance of the BOD method in this study was dependent on the uniformly good response of the wide variety of BOD seed materials. The good response was itself dependent on the easy biodegradability of the glucose-glutamic acid substrate tested. If the sample substrate was more resistant to bacterial oxidation, lower and more variable BOD values would have been recorded while the COD and TOC values most probably would have remain the same as reported here.

The TOC test is a relatively new instrumental method of measuring organic carbon. In this study it had a significant bias at lowest level tested. Further study of the TOC method and increased standardization of techniques should result in greater accuracy and precision, especially at the lower levels of oxygen demand (less than 10 mg/liter).

Ratios between COD, BOD and/or TOC can be developed easily for these sets of data on a single sample. However, a ratio is not reported because it is not applicable to any other sample. It is not possible to measure oxygen demand using one of these parameters, and by use of a precalculated ratio to determine the relative value for either of the other two parameters for another sample.

REFERENCES

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5. *Methods for Chemical Analysis of Water and Wastes*, Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, 1971.

6. *Annual Book of ASTM Standards*, Part 23, Water: Atmospheric Analysis, 1970, p. 712, American Society for Testing and Materials, Philadelphia, Pa.

APPENDIX

Raw Data Summary

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METHOD & PERFORMANCE EVALUATION, AOCL
METHOD STUDY 3, DEMAND ANALYSES

COD, SAMPLE 1

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 12.3

NUMBER OF LAB/ANALYST		INCREMENT RECOVERY BY LAB.
101	1	10.1
101	2	11.3
102	1	11.4
103	1	6.3
106	1	7.8
106	2	8.0
107	1	11.3
107	2	12.3
109	1	22.8
109	2	22.9
109	3	13.4
110	1	12.9
110	2	11.2
110	3	11.6
112	1	16.6
113	2	11.6
115	1	18.9
117	1	12.2
120	1	8.1
121	1	12.6
122	1	6.8
123	1	12.4
123	2	15.4
124	1	12.5
124	2	12.5
127	1	11.3
128	1	14.6
128	2	13.0
130	1	11.7
131	1	11.0
133	1	12.3
137	1	5.8
138	1	12.5
140	1	10.7
140	2	10.9
148	1	14.1
148	2	17.8
149	1	13.1
150	1	11.5
151	1	14.8
152	1	14.8
152	2	15.2
153	1	11.3
153	2	11.4
153	3	11.4
153	4	10.7
153	5	10.4
153	6	10.8
154	1	13.9
155	1	17.4
156	1	7.3
157	1	12.2
158	1	12.6
160	1	6.7
160	2	17.2
160	3	10.8
160	4	9.8
160	5	9.6
161	1	4.0
162	1	1.2R
163	1	13.2
163	2	12.7
164	1	10.2
165	1	26.5R
166	1	12.0
167	1	10.0
168	1	21.7
169	1	12.8
170	1	14.3
170	2	16.9
170	3	11.7
170	4	12.0
171	1	6.2
171	2	12.0
171	3	24.0R
172	1	9.4
173	1	7.4
175	1	10.7
176	1	19.4
177	1	9.9
179	1	12.5
180	1	12.2
180	2	12.5
180	3	12.2
181	1	12.0
187	1	10.2

R = REJECTED DATA.

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METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

COD, SAMPLE 2

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 270.

NUMBER OF LAB	ANALYST	INCREMENT RECOVERY BY LAB.	NUMBER OF LAB	ANALYST	INCREMENT RECOVERY BY LAB.
101	1	253.	153	5	259.
101	2	248.	153	6	263.
102	1	267.	154	1	262.
103	1	257.	155	1	275.
106	1	205.R	156	1	215.R
106	2	208.R	157	1	264.
107	1	270.	158	1	262.
107	2	265.	160	1	198.R
109	3	256.	160	2	274.
110	1	222.R	160	3	250.
110	2	264.	160	4	276.
110	3	220.R	160	5	279.
112	1	272.	161	1	258.
113	2	240.	162	1	250.
117	1	274.	163	1	255.
120	1	260.	163	2	255.
121	1	264.	164	1	253.
122	1	289.	165	1	286.
123	1	260.	166	1	263.
123	2	238.	167	1	268.
124	1	246.	168	1	257.
124	2	260.	169	1	257.
127	1	239.	170	1	302.
128	1	261.	170	2	251.
128	2	267.	170	3	269.
130	1	265.	170	4	267.
131	1	264.	171	1	263.
133	1	258.	171	2	265.
136	1	266.	171	3	264.
138	1	263.	172	1	245.
140	1	253.	173	1	261.
140	2	257.	175	1	221.R
140	3	237.	177	1	259.
148	1	269.	179	1	243.
148	2	277.	180	1	268.
150	1	260.	180	2	267.
151	1	261.	180	3	279.
152	1	264.	181	1	269.
152	2	264.	187	1	267.
153	1	252.			
153	2	244.			
153	3	254.			
153	4	253.			

R = REJECTED DATA.

METHOD & PERFORMANCE EVALUATION, AOCL
METHOD STUDY 3, DEMAND ANALYSES

BOD, SAMPLE 1

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM SEEDED WATER

INCREMENT = 2.2

NUMBER OF LAB/ANALYST		INCREMENT RECOVERY BY LAB.
101	1	2.0
101	2	2.0
102	1	2.8
103	1	2.3
106	1	2.0
106	2	1.0
107	1	2.3
107	2	1.9
110	3	2.1
112	1	2.4
113	1	2.2
113	2	2.2
115	1	3.7
117	1	2.6
121	1	2.2
122	1	1.8
123	1	2.6
123	2	2.5
124	1	2.0
124	2	2.0
128	1	1.6
128	2	1.0
130	1	2.0
133	1	1.1
136	1	1.6
137	1	0.3R
140	1	2.7
140	2	2.1
140	3	2.0
148	1	1.4
148	2	1.5
149	1	2.0
151	1	3.5
152	1	2.4
152	2	2.1
152	3	1.8
154	1	2.2
155	1	1.6
156	1	2.0
157	1	2.6
158	1	1.7
160	1	2.1
160	2	2.0
160	3	1.9
160	4	1.8
160	5	1.9
161	1	2.5
163	1	1.3
163	2	1.0
164	1	2.3
165	1	3.2
166	1	2.2
167	1	2.4
168	1	2.0
169	1	1.2
170	1	1.8
170	2	2.2
170	3	1.8
170	4	2.3
171	1	2.3
171	2	2.3
171	3	1.6
172	1	3.0
173	1	2.5
175	1	5.8R
176	1	1.6
177	1	2.4
179	1	1.5
180	1	2.3
180	2	2.3
180	3	2.1
183	1	2.2
187	1	2.5
188	1	2.6

R = REJECTED DATA.

METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

BOD, SAMPLE 2

ALL DATA, ALL LABORATURIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM SEEDED WATER

INCREMENT = 194.

NUMBER OF LAB	ANALYST	INCREMENT RECOVERY BY LAB.
101	1	190.
101	2	183.
102	1	169.
103	1	123.R
106	1	159.
106	2	145.
107	1	189.
107	2	185.
110	3	205.
112	1	198.
113	1	200.
113	2	172.
117	1	142.
120	1	152.
121	1	183.
122	1	175.
123	1	150.
123	2	191.
124	1	207.
124	2	192.
127	1	224.
128	1	218.
128	2	205.
130	1	165.
133	1	107.R
136	1	155.
138	1	223.
140	1	205.
140	2	225.
140	3	121.R
148	1	185.
148	2	181.
150	1	180.
151	1	169.
152	1	170.
152	2	171.
152	3	185.
154	1	155.
155	1	168.
156	1	171.
157	1	200.
158	1	174.
160	1	191.
160	2	197.
160	3	193.
160	4	194.
160	5	179.
161	1	130.
163	1	197.
163	2	188.
164	1	159.
166	1	182.
167	1	154.
168	1	120.R
169	1	146.
170	1	175.
170	2	179.
170	3	203.
170	4	172.
171	1	205.
171	2	180.
171	3	118.R
172	1	167.
173	1	135.
176	1	165.
177	1	201.
179	1	132.
180	1	164.
180	2	173.
180	3	160.
183	1	192.
187	1	174.
188	1	183.

R = REJECTED DATA.

METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

TOC, SAMPLE 1

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 4.9

NUMBER OF LAB	ANALYST	INCREMENT RECOVERY BY LAB.
101	1	6.5
101	2	6.3
102	1	5.0
103	1	6.4
106	1	5.0
106	2	5.0
107	1	5.0
107	2	5.0
109	1	5.0
109	2	6.0
109	3	6.0
110	1	4.3
112	1	4.5
115	1	14.0R
120	1	7.0
121	1	5.0
122	1	5.7
123	1	4.2
123	2	5.0
127	1	4.7
140	1	3.8
151	1	5.0
158	1	4.0
163	1	7.2
163	2	6.5
179	1	5.4
183	1	5.0

R = REJECTED DATA.

METHOD & PERFORMANCE EVALUATION, AQCL
METHOD STUDY 3, DEMAND ANALYSES

TOC, SAMPLE 2

ALL DATA, ALL LABORATORIES
MANUAL PROCEDURE
RECOVERY OF INCREMENT FROM DISTILLED WATER

INCREMENT = 107.

LAB	NUMBER OF ANALYST	INCREMENT RECOVERY BY LAB.
101	1	108.
101	2	106.
102	1	110.
103	1	110.
106	1	107.
106	2	107.
107	1	112.
107	2	110.
109	1	110.
109	2	110.
109	3	114.
110	1	103.
112	1	107.
120	1	127.R
121	1	106.
122	1	107.
123	1	104.
123	2	100.
127	1	110.
140	1	102.
151	1	94.
158	1	117.
163	1	105.
163	2	104.
179	1	110.
183	1	110.

R = REJECTED DATA.